Fibril formation of PIC – A mechanistic study based on SLS/DLS and UV-Vis

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Pseudoisocyanine chloride (PIC) is a prominent example of a dyestuff, which is capable of forming so-called J-Aggregates. The characteristics of this dyestuff were already investigated by Scheibe in 1937[1]. Solutions of PIC in aqueous NaCl reveal a sharp absorption band (J-Band) together with a strong fluorescence signal. Further experiments provide evidence for the existence of fibrillar entities. The most recent work suggests a subunit consisting of two strands of oppositely oriented molecules. Six of these double strands are forming a supramolecular fibril[2]. The self-assembly depends on concentration and temperature. The first step of the aggregation is the dimerization of monomers[3]. Yet, further kinetic features of the overall process are unknown.
The present work shall investigate the aggregation process of the dyestuff as a function of concentration, temperature and additional salts. With time resolved static and dynamic light scattering (SLS/DLS) the temporal evolution of aggregation was recorded in detail for the first time. Time resolved SLS/DLS reveals, the weight averaged molar mass M_w, the radius of gyration R_g and the hydrodynamically effective radius R_h, which quantifies the extent of aggregation and which makes possible to describe the size and shape of aggregates during the process (Fig.1 left). Additionally, UV-Vis experiments were carried out to analyse the sample composition in terms of monomers/dimers/aggregates (Fig. 1 right). All experiments were conducted either in pure water or in aqueous salt solutions with NaCl, NaBr or NaAc at a fixed salt concentration of 0.01M to reveal the impact of salts on self-assembly. The comparable topology of PIC and amyloid aggregates and the easy handling of PIC solutions together with a great reproducibility of the experiments makes the dyestuff a powerful model system for such protein self-assembly.

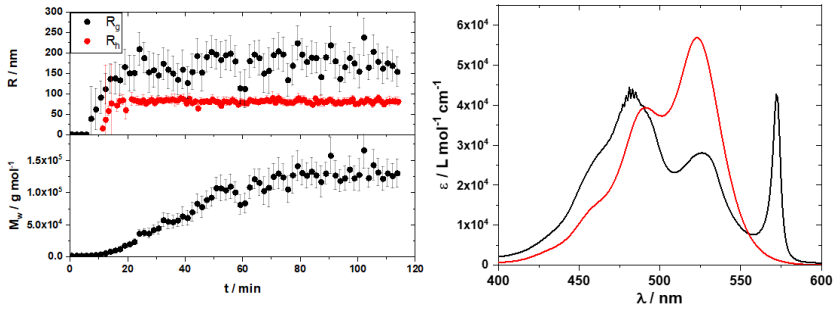

Figure 1. Left: Temporal evolution of the parameters obtained by SLS/DLS. Aggregation was induced by a temperature jump of ΔT = 1°C. Right: UV-Vis spectra of monomeric PIC (red) and aggregated PIC (black). Since these spectra are a superposition of monomer, dimer and aggregates spectra, quantification of the composition is possible.

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